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ENGINEERING DATA TRANSMITTAL

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1	RPP-14841	N/A	0	Organic Vapor Source Term for Tanks 241-C-201, 241-C-202, 241-C-203 and 241-C-204 During Waste Retrieval Operations	E/Q	1		

16. KEY

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		Design Agent									
1	1	Cog. Eng. J.H.E. Rasmussen	[signature]	3-21-03							
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1	1	Env. C.J. Kemp	[signature]	3-21-03							

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[signature] 3-21-03 JHE Rasmussen — Signature of EDT Originator / Date	Authorized Representative for Receiving Organization / Date	[signature] M.A. Knight 3/24/03 — Design Authority/ Cognizant Manager / Date	Ctrl No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments

EDT. 636124
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Design Review Checklist for Simple Designs/Simple Design Changes (Routine Engineering Change Notices)

Subject: RPP-14841

Originator: Juergen H. E. Rasmussen (Print/Sign) JRasmussen Date: 3-24-03

Checker: Daniel A. Reynolds DAReynolds **Date:** 3/24/03

This document consists of 24 pages and the following attachments (if applicable):
Attachment A ✓
Attachment B ✓

Documents/Engineering Change Notices Reviewed:

Affected Document(s) (Optional):

Yes	No	N/A	
[X]	[ ]	[ ]	Were the design inputs correctly selected?
[X]	[ ]	[ ]	Are assumptions necessary to perform the design activity adequately described and reasonable?
[X]	[ ]	[ ]	Where necessary, are the assumptions identified for subsequent re-verifications when the detailed design activities area completed?
[X]	[ ]	[ ]	Was an appropriate design method used?
[X]	[ ]	[ ]	Were the design inputs correctly incorporated into the design?
[X]	[ ]	[ ]	Is the design output reasonable compared to design inputs?
[X]	[ ]	[ ]	Are the necessary design input and verification requirements for interfacing organizations specified in the design documents or in supporting procedures or instructions?

Checklist Completed By: Daniel A. Reynolds DAReynolds (Print/Sign) Date: 3/24/03

DISTRIBUTION SHEET

To	From	Page 1 of 1
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Project Title/Work Order		EDT No. EDT-636124
RPP-14841, Rev. 0, "Organic Vapor Source Term for Tanks 241-C-201, C-202, C-203 and C-204 During Waste Retrieval Operations"		ECN No. N/A

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Organic Vapor Source Term for Tanks 241-C-201, 241-C-202, 241-C-203 and 241-C-204 During Waste Retrieval Operations

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Abstract: Tanks 241-C-101, 202, 203 & 204 waste will be retrieved & transferred to tank 241-AY-101 prior to transfer to the Waste Treatment Plant. The purpose of this study is to determine an organic emission source term for retrieval & transfer of sludge from the C-200 tanks to 241-AY-101. This study showed that emissions of organic compounds from retrieving the C-200 tanks would be below WAC regulations for Acceptable Source Impact Level that indicates abatement systems are not required.

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ORGANIC VAPOR SOURCE TERM FOR TANKS 241-C-201, 241-C-202, 241-C-203, AND 241-C-204 DURING WASTE RETRIEVAL OPERATIONS

J. H. E. Rasmussen
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EXECUTIVE SUMMARY

The River Protection Project mission is to safely store, retrieve, treat, immobilize, and dispose of the Hanford Site tank waste. A key part to meeting the River Protection Project mission is the successful retrieval of waste from selected tanks including tanks 241-C-201, 241-C-202, 241-C-203, and 241-C-204 (C-200 tanks).

The C-200 tank waste will be retrieved and transferred to the Double-Shell Tank (DST) System prior to transfer to the Waste Treatment Plant. The purpose of this study is to determine an organic emission source term for retrieval and transfer of sludge from the C-200 tanks to the DST System.

This study showed that emissions of organic compounds from retrieving the C-200 tanks would be below Washington Administrative Code regulations for Acceptable Source Impact Level that indicates that abatement systems are not required. The use of the simple screening model described in this document indicates that no compounds could exceed Washington Administrative Code regulations for Small Quantity Emission Rates.

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LIST OF TERMS

AMS	Articulated Mast System
ASIL	Acceptable Source Impact Level
CAS	Chemical Abstract Service
cfm	cubic feet per minute
DST	Double-Shell Tank
g/mg	grams per milligram
g/s	grams per second
kg	kilograms
lb/hr	pounds per hour
lb/yr	pounds per year
m^3/hr	cubic meters per hour
mg/m^3	milligram per cubic meter
MRS	Mobile Retrieval System
PNNL	Pacific Northwest National Laboratory
ppb	part per billion
ppbv	part per billion volume
PUREX	plutonium-uranium extraction
SAS	Special Analytic Support

LIST OF TERMS, Continued

SQER	Small quantity emission rates
TAP	Toxic Air Pollutants
TST	Triple Sorbent Tubes
TWINS	Tank Waste Information Network System
$\mu g/m^3$	microgram per cubic meter
VOC	volatile organic compounds
WAC	*Washington Administrative Code*

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1.0 INTRODUCTION

The U.S. Department of Energy, Office of River Protection (ORP) mission is to safely store, retrieve, treat, immobilize, and dispose of the Hanford Site tank waste. A key part to meeting the ORP mission is the successful retrieval of waste from selected tanks and timely delivery of that waste to the Waste Treatment Plant (WTP) immobilization facilities.

Retrieval of waste from tanks to supply feed to the WTP is scheduled to begin in 2004. Tanks 241-C-201, 241-C-202, 241-C-203, and 241-C-204 (C-200 tanks) contain sludge, which will be retrieved for high-level waste (HLW) feed activities, as part of the Waste Feed Delivery (WFD) project. The recent Mission Acceleration plan has scheduled waste from the C-200 tanks to be retrieved in late Fiscal Year (FY) 2003 or early in FY 2004 and transferred to the Double-Shell Tank (DST) system where it will be combined with other waste staged for final treatment.

The current tank C-200 tanks retrieval project baseline uses the Mobile Retrieval System (MRS) which consists of an In-Tank Vehicle that can push or jet waste to an Articulating Mast System (AMS) which vacuums out the waste with pneumatic assisted conveyance to an above grade vessel skid. The In-Tank Vehicle portion of the MRS will not be utilized for the C-200 tanks. From the vessel skid, the waste will be transferred to the DST System. The purpose of this document is to determine an organic pollutant source term for retrieval of the C-200 tank sludge.

2.0 SCOPE

This study determined an organic pollutant source term for retrieval of the C-200 tanks. The source term was then compared to *Washington Administrative Code* (WAC) 173-400 and 173-460 regulations.

3.0 BACKGROUND

The C-200 tanks share similar processing histories and waste types and are, therefore, expected to exhibit comparable organic pollutant emissions during retrieval activities. The C-200 tanks received uranium metal waste during the 1940's, and were sluiced out in the 1950's. During the 1960's, the C-200 received wastes from the Hot Semiworks facility, including small batches of waste from actinide and fission product separations processes being developed for B-Plant and plutonium-uranium extraction (PUREX). Some of these wastes contain solvent extraction residues originating in these separations processes. The supernatant liquids have been removed from the C-200 tanks, and the tanks now contain shallow sludge layers (predicted to be 7,000 gallons total volume from all four tanks).

Organic pollutants in a tank's headspace derive from the organic compounds contained in the tank waste. The organic compounds in the tank waste produce organic pollutants in the tank headspace by evaporation, hydrolysis, and by radiolysis. No aqueous supernatant layer exists to trap water-insoluble pollutants in the C-200 tank sludge. The tanks are not actively ventilated. The shallow sludge layers are believed to be in equilibrium with the headspace gases and vapors.

4.0 METHODOLOGY

An EXCEL®[1] spreadsheet was developed to determine the pollutant source term. Verification of the spreadsheet is provided in Appendix B. The Chemical Abstract Service (CAS) number is the common reference for compounds because many compounds have several different names but only one CAS number. Limited characterization data are available for the C-200 tanks; therefore, a bounding pollutant source term was developed by comparison with tanks 241-C-104 and 241-C-106.

Limited condensed phase and vapor phase characterization data are available for the C-200 tanks. Condensed phase data for tanks 241-C-201 (C-201), 241-C-202 (C-202), and 241-C-203 (C-203) are limited to inorganic and organic salts, total organic carbon, moisture, radionuclides, and physical properties. The condensed phase samples of tank 241-C-204 (C-204) consist of an oily sludge phase associated with a rag that was retrieved by the auger-sampling device and, therefore, is not considered to be representative of the sludge layer as a whole, but does provide some insight into the pollutants that may be present. The primary organic constituent of the oily sludge from the rag obtained from tank C-204 rag sample was tributyl phosphate (Conner 1996).

Extensive vapor characterization of the C-200 tank headspaces was performed only for tank C-204. Vapor phase data for tanks C-201 and C-202 are limited to permanent gases, ammonia, total non-methane hydrocarbon (TNMHC), and water vapor. The vapor phase of tank C-203 was surveyed by portable flammability detection instruments.

The Articulated Mast System (AMS) will be used to retrieve the sludge layer of each tank. The AMS consists of a TORE™[2] cyclonic pick-up device, and a pneumatic conveying tube that will transport the retrieved waste to an above-grade skid-mounted vacuum tank. A vacuum pump with a capacity of 500 cubic feet per minute (cfm) will maintain a vacuum of up to 25 inches of mercury (in. Hg) in the vacuum tank and exhaust the pneumatic conveying air back into the tank headspace.

Sludge will be retrieved from the C-200 tanks using the MRS. The TORE™ pickup device entrains and suspends particulates and sludges in a turbulent air stream. The entrained waste is conveyed pneumatically through a tube to an above-grade vacuum tank, where the solids and sludges will be disengaged from the conveying air. The particulates and sludges will be in intimate contact with the conveying air in the TORE™ device, conveying tube, and vacuum tank

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[1] EXCEL® is a registered trademark of Microsoft, Redmond, Washington.
[2] TORE is a trademark of Non-Entry Systems, Limited.

during retrieval operations. It is, therefore, reasonable to assume that the conveying air exhausted from the vacuum tank will be saturated with each organic constituent in the waste at its respective vapor pressure in the waste matrix. If the vacuum pump operates for an extended period without fresh waste being added to the vacuum tank, some of the more volatile constituents may become depleted.

It is assumed that the sludge is currently in equilibrium with the tank headspace in each of the C-200 tanks. Therefore, the tank C-204 headspace samples are used to represent the equilibrium vapor pressure of each organic pollutant in the sludge. In order to provide a bounding estimate of pollutant emissions during retrieval, it is assumed that the MRS will contact the sludge with the conveying air, and that the 500 cfm exhausted from the vacuum tank will contain the same partial pressures of organic compounds as was found in tank C-204 headspace samples. Mass transfer and depletion of organic pollutants from the sludge make the actual pollutant concentrations less than those assumed. The vacuum pump capacity will decrease with increasing vacuum in the vacuum tank, making the assumed 500-cfm flowrate bounding. It is further assumed that the chemical concentrations measured in tank C-204 will bound the concentrations in tanks C-201, C-202, and C-203.

The chemical release rate was assumed based on a draft process flow sheet for retrieval of the C-200 tanks and subsequent emissions were calculated. These concentrations were then compared to emission limits from the WAC 173-400 and WAC 173-460.

4.1 SPREADSHEET

An EXCEL® spreadsheet, containing multiple worksheets, was developed to determine the Volatile Organic Compound (VOC) source term. Each worksheet performed a specific function as detailed in Appendix B. Some worksheets collected data from various sources such as the Tank Waste Information Network System (TWINS) database and the Washington Administrative Code (WAC). Other worksheets performed calculations on the data. Worksheet "C204 data" collects data from TWINS (2003a). Worksheet "C204 calc" determines an emission rate from the data contained in "C204 vapor data." Worksheet "173-460-160" lists regulatory information directly from WAC 173-460-160 for class B Toxic Air Pollutant (TAP) and Acceptable Source Impact Levels (ASIL). Worksheet "Regulated compounds" compiles all of the regulated compounds from various WAC codes and sorts the compounds by the CAS number. Worksheet "Source term emission limit ratio" compares the calculated emission rates with applicable regulatory limits.

4.2 BASIS OF MODEL

Because the chemistry in the Hanford Site waste tanks is far too complex to model thermodynamically for pollutant emission calculation, an empirical model was developed. Representative condensed phase sample data are not available for volatile and semivolatile organic constituents of the C-200 tanks. Measurements of organic vapor-phase constituents are available only for tank C-204. It was assumed that the pollutant concentrations in all four C-200 tanks could be represented by tank C-204 headspace vapor measurements.

Vapor samples were collected from tanks C-201, C-202, and C-204 in June and July 1996 using the In Situ Vapor Sampling (ISVS) system. The ISVS system uses a bundle of sorbent trap sampling devices that is lowered into the tank headspace. Metered amounts of headspace air are drawn through each set of sorbent traps, which are then sent to a laboratory for analysis. Replicate samples were collected, and selected samples were subject to replicate analyses. Samples collected from tanks C-201 and C-202 were not analyzed for specific organic species because analyses of their total non-methane hydrocarbon concentrations were below levels of concern.

High levels of the semivolatile alkanes in the headspace of tank C-204 are consistent with the auger samples, which indicated the tank may contain a separate organic liquid waste phase. Comparing the measured semivolatile organic vapor concentrations to their calculated vapor pressures using Raoult's law indicates these species are essentially in equilibrium with the organic liquid phase. This is not unreasonable; given tank C-204 is passively ventilated and has no significant air pathways besides its breather filter, it would be expected to have a very low ventilation rate (Huckaby et al. 1998), and vapors are expected to be nearly in equilibrium with liquids present. Similar calculations indicated the semivolatile organic vapors in tank 241-C-103 (which is also passively ventilated) to be at equilibrium with the organic liquid in that tank.

In-tank photographs indicate that the oily sludge phase noted in the rag retrieved by the tank C-204 auger sample is localized. It is, therefore, conservative to assume that the organic vapor concentrations in the tank headspace bound organic emissions which will occur when other, less organic-rich portions of the waste from tank C-204 are retrieved. Review of the total non-methane hydrocarbon (TNMHC) results for tank C-201 and tank C-202 indicates that the organic emissions from tank C-204 will bound the emissions from the remaining C-200 tanks. No information is available about individual organic pollutants in the other C-200 tanks.

In this emission review, depletion of volatile constituents from the waste was neglected. It is assumed that the vacuum pump operates continuously for a full year, exhausting organic pollutants at the concentrations observed in the static tank C-204 vapor samples. This approach is valid to the extent that the organic chemical contents of tanks C-201, C-202, and C-203 are bounded by tank C-204. It is assumed that no significant organic pollutants are trapped in the waste that were not in communication with the tank headspace at the time of sampling.

Organic pollutant release concentrations were calculated assuming that 900 m^3/hr (530 cfm) of air containing the pollutant concentrations observed in tank 241-C-204 are exhausted year-round during the retrieval of the C-200 tanks. The mean concentrations were increased by 2 times the standard deviation to reflect statistical variability in the results. These emissions were then compared to regulatory limits.

The ammonia emissions from the C-200 tanks were estimated in the same way as the organic pollutants. No condensed phase ammonia concentrations were measured for the C-200 tanks. Ammonia was nondetectable in the headspaces of tanks C-201 and C-202. No ammonia measurements were performed for the tank C-203 headspace. Ammonia was only detected in two headspace samples from tank C-204. The mean of the two detected ammonia results was increased by two standard deviations to reflect statistical uncertainty. Ammonia emissions were calculated by assuming that this concentration was emitted year-round at 900 m^3 per hour during retrieval of the C-200 waste. As with the organic emissions estimate, these assumptions are conservative in that the actual vacuum pump capacity decreases with increasing vacuum, ammonia will gradually be depleted from the waste in the vacuum tank, the ammonia concentrations in the other C-200 tanks are less than in tank C-204, and the retrieval activity will take considerably less than a year.

5.0 ASSUMPTIONS

A number of simplifying assumptions were made to complete this study. Important assumptions are listed below along with the basis for the assumption. More detailed assumptions are documented as part of the spreadsheet.

1. Average organic vapor concentrations were increased by 2X standard deviation or, if not available, by 20 percent.

   Basis: This is a conservative assumption. Two times the Standard Deviation should represent a 95 percent confidence that the actual concentration is bounded. Combining this with the other conservative assumptions provides good confidence that the emissions are bounded.

2. All of the sludge in the C-200 tanks has an equilibrium vapor pressure that results in vapor space concentrations equal to that measured in the tank C-204 headspace samples.

   Basis: Tank C-204 had higher total non-methane organic compounds (TNMOC) and ammonia concentrations than tanks C-201 and C-202. The shallow sludge layers are shallow, and are not likely to contain regions with elevated organic concentrations that do not communicate with the headspace. At the very low passive ventilation rates in the C-200 tanks, the headspace vapors are essentially in equilibrium with the sludge.

3. Organic vapor and ammonia emissions are the product of the vacuum pump flow rate and the equilibrium vapor pressure.

   Basis: The TORE™ unit and pneumatic conveying system provide intimate contact between the conveying air and the sludge. The entire conveying air stream is exhausted from the vacuum tank by the vacuum pump. Even if the C-200 tanks or receiver tank were actively ventilated during retrieval, other air streams passing through the headspace will not be as effectively contacted with the sludge as the pneumatic conveying air exhausted by the vacuum pump.

4. The quantity of air saturated with organic pollutants at the waste matrix vapor pressure is 900 m^3/hr (530 cfm).

   Basis: Preliminary vendor data includes a pump curve with a maximum of approximately 900 m^3/hr. Preliminary flowsheets indicate that the vacuum pump will exhaust 470 cfm. Communications with project personnel indicate that the capacity of the pump tentatively selected for this retrieval is 500 cfm. The vacuum pump skid will contain two such pumps in parallel, but only one will be operated at a time. The value of 900 m^3/hr was selected to bound the likely values. The flowrate can be tripled without exceeding any emissions limits.

6.0 REGULATED POLLUTANT EMISSIONS

6.1 CRITERIA POLLUTANTS

Criteria Pollutants are regulated under WAC 173-400-110. Exemption thresholds are listed in WAC 173-400-110(5)(d) in Table 6-1.

Table 6-1. Pollutant Threshold Level (Tons per Year).

(a) Total Suspended Particulates	1.25
(b) PM-10	0.75
(c) Sulfur Oxides	2.0
(d) Nitrogen Oxides	2.0
(e) Volatile Organic Compounds, total	2.0
(f) Carbon Monoxide	5.0
(g) Lead	0.005
(h) Ozone Depleting Substances (in effect on July 1, 2000), total	1.0
(i) Toxic Air Pollutants	As specified in chapter 173-460 WAC.

If these thresholds are not exceeded, permitting is not required. Table 7-2 demonstrates that these thresholds are not exceeded for item (i).

This study did not analyze emissions for Total Suspended Particulates, PM-10, Sulfur Oxides, Nitrogen Oxides, Volatile Organic Compound total, Carbon Monoxide, Lead, or Ozone Depleting Substances. These pollutants are typically generated as combustion products, and the Hanford Site waste tanks are not a significant source. Retrieval of the C-200 tanks will not involve a combustion-powered generator.

6.2 HAZARDOUS POLLUTANTS

Hazardous air pollutants are regulated by WAC 173-401. Emission levels of these pollutants determine the basis of significant versus insignificant for Air Operating Permit purposes. None of the hazardous air pollutants exceeds threshold limits as shown in the last column of Table 7-2.

6.3 TOXIC AIR POLLUTANTS

Toxic Air Pollutants (TAP) are regulated in WAC 173-460. Permits are not required if TAP emissions are below the small quantity emission rates (SQERs). If emissions are above the SQER, but still below acceptable source impact levels (ASILs), control technologies are not necessary. The ASILs are concentrations seen by members of the public at the site boundary. The SQERs are emissions just out of the stack.

None of the TAPs identified in the C-200 tanks exceed the SQER during the simple screening done by multiplying the vapor concentration by vacuum pump flowrate. None of these TAPs exceeded the ASIL.

Per WAC 173-460, TAPs are divided into two classes for regulatory purposes. Class B compounds are regulated on a 24-hour average. Class A compounds are typically regulated on an annual average (Class AII in Table A-1). Selected Class A compounds are regulated on a 24-hour average (Class AIII in Table A-1).

The ASIL ratio listed in Table 7-2 applies unit concentration factors to stack concentrations to compensate for distance from the tank farms to the public and for wind velocities (May 2000 Appendix C). No C-200 tank TAPS have a ratio greater that 1 for ASIL dispersed, and do not exceed WAC 173-460 limits.

7.0 POLLUTANT SOURCE TERM

This section explains the origin of pollutant in the tank headspace, describes the sources of data used, and provides an estimate of the pollutant source term.

7.1 ORIGIN OF VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compounds in a tank's headspace derive from the organic compounds contained in the tank waste. Some of sludge in the C-200 tanks originated in solvent extraction separation processes employed at Hot Semiworks. The Hot Semiworks processed small batches of radioactive process solutions to support fission product and actinide separation process development for large-scale use at B-Plant and PUREX. The sludge remaining in the C-200 tanks contains residues of these processing solvents remained in the C-200 tanks. The solvent residues produce pollutants in the tank headspace by evaporation, hydrolysis, and radiolysis. Much more information on pollutant origin is contained in Stauffer (1999).

7.2 DATA SOURCE FOR POLLUTANT

Data used to develop a non-radioactive chemical source term came from primarily from the TWINS vapor characterization analysis report (TWINS 2003a), the Waste Tank Summary Report (Hanlon 2002), the *Origin of Volatile Organic Compounds Emerging from Tank 241-C-106* (Stauffer 1999), and preliminary retrieval flowsheet information as described below.

7.2.1 TWINS Vapor Characterization Analysis Report

The TWINS vapor characterization analysis report (TWINS 2002a) contains substantial information about vapor space concentrations of ammonia and pollutants. The laboratory analyses contained in the report are validated. Data qualifiers are added to provide information about the quality of the vapor result data. For this study, data tagged with the qualifier "X" was utilized even though this data did not have approved quality assurance documentation or significant quality assurance deficiency was associated with the reported result. Compounds listed as tentatively identified were also included even though standards were not used for these compounds.

Vapor samples were collected from tanks C-201, C-202, and C-204 in June and July 1996 using the In Situ Vapor Sampling (ISVS) system. The ISVS system uses a bundle of sorbent trap sampling devices that is lowered into the tank headspace. Metered amounts of headspace air are drawn through each set of sorbent traps, which are then sent to a laboratory for analysis. Replicate samples were collected, and selected samples were subject to replicate analyses. Samples collected from tanks C-201 and C-202 were not analyzed for specific organic species because analyses of their total non-methane hydrocarbon concentrations were below levels of concern.

High levels of the semivolatile alkanes in the headspace of C-204 are consistent with the auger samples, which indicated the tank contains a separate organic liquid waste phase. Comparing the measured semivolatile organic vapor concentrations to their calculated vapor pressures using Raoult's law indicates these species are essentially in equilibrium with the organic liquid phase. This is not unreasonable; given tank C-204 is passively ventilated and has no significant air pathways besides its breather filter it would be expected to have a very low ventilation rate (Huckaby et al. 1998), and vapors would be expected to be nearly in equilibrium with liquids present. Similar calculations indicated the semivolatile organic vapors in tank 241-C-103 (which is also passively ventilated) to be at equilibrium with the organic liquid in that tank.

Cyanide was not reported in the headspace sample results. The equivalent cyanide content of the tank C-204 samples was calculated from the results for propane nitrile, butane nitrile, hexane nitrile, and heptane nitrile.

7.2.2 Waste Tank Summary Report

The Waste Tank Summary Report (Hanlon 2002) lists tank contents by waste type. This document is based on the Best-Basis Inventory (BBI), which represents the best possible estimates of the tank contents, and they are used consistently throughout the Hanford Site technical community.

7.2.3 Tank 241-C-106 Source Term Data

The C-200 tank organic pollutants will differ from those experienced during tank 241-C-106 retrieval. The C-200 tanks are passively ventilated and solvent residues are not trapped beneath aqueous supernatant layers as was the case in tank 241-C-106. The C-200 tank sludge layers are thin, and are believed to be in equilibrium with the headspace vapors. The C-200 tank sludges will be retrieved by the MRS, and the tank 241-C-106 sludge was retrieved by sluicing. Therefore, the distribution of organic pollutants and the mechanism for generating emissions differs from that in tank 241-C-106. However, the sludge chemistry and mechanisms for generating organic pollutants in the C-200 tanks have much in common with tank 241-C-106.

Significant work has been done on the pollutant source term during sluicing of tank 241-C-106 both before sluicing and during sluicing (Stauffer 1999). Samples from the dome space of quiescent tank 241-C-106 had been collected and analyzed by Rasmussen (1994), Jenkins et al. (1994), and Ma et al. (1997). Based upon these sampling events, it has been established that there were many different organic compounds at low concentration in the dome space of the tank years prior to beginning sluicing. Acetone, butanol, the heptenes, and the heptanones were more abundant than the other organic compounds that included alkanes, alkenes, alcohols, aldehydes, ketones, and nitriles.

Six samples were collected from the ventilation stack of tank 241-C-106 before the initiation of sluicing operations on December 16, 1998, and March 7, 1999. These samples also contained many different organic compounds including the same alkanes, alkenes, alcohols, aldehydes, ketones, and nitriles observed in the work from previous years. The concentrations of many of these substances did not exceed 5 parts per billion (ppb) prior to sluicing and several of them were detected in only one of the six samples.

Huckaby and Evans (1999) found that samples, which were opportunistically collected from the ventilation stack of tank 241-C-106 during sluicing operations on November 18, 1998, contained hexane, heptane, 3-methylheptane, nonane, decane, undecane, dodecane, butylcyclopropane, 1-butyl-2-methylcyclopropane, 1-hexene, 2- and 3-heptene, several isomeric methylheptenes, and 3- and 4-heptanone.

During sluicing, approximately 25 samples were collected from the ventilation stack of tank 241-C-106 on December 16, 1998. These samples were analyzed at Pacific Northwest National Laboratory (PNNL) (Huckaby and Evans 1999) and at Special Analytic Support (SAS) (Bonfoey et al. 1999a). Samples were also collected during sluicing operations on March 7, 1999. These samples were analyzed at SAS (Bonfoey et al. 1999b). The 10 samples, which were collected on March 28, 1999, were also analyzed at SAS (Bonfoey et al. 1999c).

The extensive results assembled in the data packages show that the observations reported by PNNL and by SAS for the triple sorbent tubes (TST) and SUMMA[3] canisters, which were collected at about the same time on December 16, 1998, were similar. The results for the TST and SUMMA canisters collected at about the same time on March 7 and March 28, 1999 were also quite similar.

Three samples that had been collected in SUMMA canisters during active sluicing operations on December 16, 1998, March 7, 1999, and March 28, 1999 were examined thoroughly. Pure compounds were employed to resolve uncertainties about the identification of isomeric compounds, for example, by specifically comparing the chromatographic signals of pure E- and Z-2-heptene, E- and Z-3-heptene, and distinguishing between alkadienes and cycloalkenes. The identities of about 40 of tentatively identified compounds were affirmed by comparison of the retention times and mass spectra of the observed constituents with the retention times and mass spectra of pure compounds. The identities of these 40 compounds and 50 target compounds, therefore, are assured. About 70 other compounds were tentatively identified.

The organic compound structures were elaborated by comparison of their retention times and mass spectra with information obtained by the study of the target analytes and reference compounds as well as with information in the chemical literature, by comparison with related results provided by PNNL, Oak Ridge National Laboratory (ORNL) and Oregon Graduate Institute (OGI), and by chemical inferences based on the original organic source term. Most of these identifications are secure, but some, for example, the positional and geometric isomers of the alkylcyclohexanes, are not assured. In some cases, substances are listed as unknown. Most of the substances in this category were present in low abundance or coeluted and their identification was hindered by their low concentrations and often by poorly defined mass spectrum. The uncertainty in the concentration of a target compound is about 30 percent (Huckaby et al. 1995, 1996). The concentrations of tentatively identified compounds are

[3] SUMMA is a trademark of Moletrics, Inc., Cleveland, Ohio.

measured by comparison of the observed ion concentration current with the ion current of an internal standard (Stauffer 1999).

7.2.4 Condensed Phase Measurements

No condensed phase measurements are available for ammonia nor volatile and semivolatile organic compounds in the C-200 tank waste except for an oily sludge phase associated with a rag retrieved from tank C-204 (TWINS 2003b). This oily sludge contained approximately 33 percent tributyl phosphate (TBP), and trace, unquantified amounts of normal paraffin hydrocarbons (decane, dodecane, and tridecane) normally associated with processing plant solvents. The rag containing this oily sludge phase is clearly not representative of the C-200 tank waste as a whole based on a review of photographs and recent videos. The waste surface in tank C-204 consists mainly of yellowish sludge with darker material visible in localized areas and cracks in the sludge surface.

7.3 ESTIMATED AMMONIA SOURCE TERM

Ammonia emissions were estimated based upon TWINS data. The ammonia emissions from the C-200 tanks were estimated from headspace concentrations. No condensed phase ammonia concentrations were measured for the C-200 tanks. Ammonia was nondetectable in the headspaces of tanks C-201 and C-202. No ammonia measurements were performed for the tank C-203 headspace. Ammonia was only detected in two headspace samples from tank C-204.

The ammonia emissions from the C-200 tanks were estimated in the same way as the organic pollutants. The mean of the two detected tank C-204 ammonia results was increased by two standard deviations to reflect statistical uncertainty. Ammonia emissions were calculated by assuming that this concentration was emitted year-round at 500 cfm during retrieval of the C-200 waste. As with the organic emissions estimate, these assumptions are conservative in that the actual vacuum pump capacity decreases with increasing vacuum, ammonia will gradually be depleted from the waste in the vacuum tank, the ammonia concentrations in the other C-200 tanks are less than in tank C-204, and the retrieval activity will take considerably less than a year.

7.4 ESTIMATED POLLUTANT SOURCE TERM

The worst-case pollutant source term for stack emissions is contained in Table 7-1. A comparison of the source term to regulatory limits for all pollutant is contained in Table 7-2.

Table 7-1. Pollutant Source Term for C-200 Tank[3] Stack Emissions. (2 sheets)

Chemical Name	Chemical ID	TAP[(1)] Class	C-200 Emissions lb/hr[(2)]	C-200 Emission µg/m³ [(2)]	C-200 Emissions ton/yr[(2)]
Ethyl benzene	100-41-4	B	2.40E-05	2.40E-07	9.54E-05
Undecane, 3-methyl-	1002-43-3		5.25E-03		2.09E-02
Butane	106-97-8	B	1.01E-03	1.01E-05	4.00E-03
1,3-Butadiene	106-99-0	AII	2.02E-03	7.11E-04	8.04E-03
Propanenitrile	107-12-0		1.76E-04		7.00E-04
Methyl isobutyl ketone	108-10-1	B	5.03E-05	5.03E-07	2.00E-04
Benzene, methyl-	108-88-3	B	3.55E-04	3.55E-06	1.41E-03
Cyclohexanone	108-94-1	B	1.83E-04	1.83E-06	7.28E-04
Pentane	109-66-0	B	8.11E-05	8.11E-07	3.23E-04
Butanenitrile	109-74-0		4.79E-04		1.90E-03
Furan, tetrahydro-	109-99-9	B	2.73E-04	2.73E-06	1.08E-03
hexane (n-hexane)	110-54-3	B	9.85E-05	9.85E-07	3.92E-04
Pentanenitrile	110-59-8		1.47E-05		5.86E-05
Cyclohexane	110-82-7	B	1.24E-04	1.24E-06	4.94E-04
Pyridine	110-86-1	B	1.11E-05	1.11E-07	4.40E-05
Octane	111-65-9	B	9.59E-05	9.59E-07	3.82E-04
Nonane	111-84-2	B	1.08E-04	1.08E-06	4.31E-04
Dodecane	112-40-3		2.56E-02		1.02E-01
Undecane	1120-21-4		7.19E-03		2.86E-02
1-Octadecanol	112-92-5		3.21E-02		1.28E-01
1-Propene	115-07-1		1.10E-03		4.39E-03
1-Propene, 2-methyl-	115-11-7		6.84E-04		2.72E-03
propionaldehyde	123-38-6		1.55E-03		6.19E-03
Butanal	123-72-8		3.99E-05		1.59E-04
Decane	124-18-5		2.15E-03		8.55E-03
Phosphoric acid tributyl ester	126-73-8	B	1.51E-04	1.51E-06	6.02E-04
Tridecane, 6-methyl-	13287-21-3		7.75E-03		3.08E-02
Heptane	142-82-5	B	1.70E-04	1.70E-06	6.75E-04
Cyanides, as CN	51-12-5	B	3.85E-04	3.85E-06	1.53E-03
Carbon tetrachloride	56-23-5	AII	2.85E-06	1.00E-06	1.13E-05
Butane, 1-nitro-	627-05-4		5.87E-03		2.34E-02
n-Propyl nitrate	627-13-4	B	2.42E-03	2.42E-05	9.65E-03
Hexanenitrile	628-73-9		2.39E-05		9.50E-05
Tridecane	629-50-5		2.60E-02		1.04E-01
Tetradecane	629-59-4		1.04E-02		4.15E-02
Ethanol	64-17-5	B	1.09E-03	1.09E-05	4.34E-03
Methanol	67-56-1	B	1.24E-03	1.24E-05	4.93E-03
2-Propanone	67-64-1	B	3.49E-03	3.49E-05	1.39E-02
Methane, trichloro-	67-66-3	AII	8.76E-06	3.08E-06	3.49E-05
1-Propanol	71-23-8	B	2.53E-03	2.53E-05	1.01E-02
1-Butanol	71-36-3	B	8.84E-03	8.84E-05	3.52E-02
Benzene	71-43-2	AII	2.37E-05	8.34E-06	9.43E-05
Ethane, 1,1,1-trichloro-	71-55-6	B	9.96E-06	9.96E-08	3.97E-05
Methane, chloro-	74-87-3	B	2.60E-05	2.60E-07	1.03E-04

Table 7-1. Pollutant Source Term for C-200 Tank[3] Stack Emissions. (2 sheets)

Chemical Name	Chemical ID	TAP[(1)] Class	C-200 Emissions lb/hr[(2)]	C-200 Emission $\mu g/m^3$[(2)]	C-200 Emissions ton/yr[(2)]
Acetonitrile	75-05-8	B	6.85E-04	6.85E-06	2.73E-03
Acetaldehyde	75-07-0	AII	5.34E-04	1.88E-04	2.13E-03
Methane, dichloro-	75-09-2	AII	1.51E-04	5.31E-05	6.01E-04
tert-Butyl alcohol	75-65-0	B	8.66E-05	8.66E-07	3.45E-04
Ethane, 1-chloro-1,1-difluoro-	75-68-3		1.82E-03		7.24E-03
Methane, trichlorofluoro-	75-69-4	B	7.72E-05	7.73E-07	3.07E-04
Methane, dichlorodifluoro-	75-71-8	B	3.88E-05	3.88E-07	1.55E-04
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	76-13-1	B	4.21E-04	4.21E-06	1.68E-03
Ammonia	7664-41-7	B	1.34E-06	1.34E-08	5.32E-06
2-Butanone	78-93-3	B	1.30E-03	1.30E-05	5.18E-03

Notes:

(1) Toxic Air Pollutant – some pollutants have no TAP class assigned
(2) Emissions from C-200 tanks are the total of the emissions from tanks C-201, C-202, C-203, and C-204.

Table 7-2. Source Term Emission Limit Ratio. (2 sheets)

Toxic Air Pollutant	Chemical ID	TAP Class	SQER A lb/yr B lb/hr	ASIL ($\mu g/m^3$) AII - Annual Average B - 24hr Average	Threshold Levels tons/year	SQER Ratio A lb/yr B lb/hr	ASIL Ratio A - Annual Average B - 24hr Average	Threshold Ratio Levels
Ethyl benzene	100-41-4	B	5	1000	0.50	0.00	0.00	0.00
Butane	106-97-8	B	5	6300		0.00	0.00	
1,3-Butadiene	106-99-0	AII	0.5	0.0036	0.035	0.00	0.20	0.23
Methyl isobutyl ketone	108-10-1	B	5	680	0.50	0.00	0.00	0.00
Toluene	108-88-3	B	5	400	0.50	0.00	0.00	0.00
Cyclohexanone	108-94-1	B	5	330		0.00	0.00	
n-Pentane	109-66-0	B	5	6000		0.00	0.00	
Tetrahydrofuran	109-99-9	B	5	2000		0.00	0.00	
hexane (n-hexane)	110-54-3	B	2.6	200	0.50	0.00	0.00	0.00
Cyclohexane	110-82-7	B	5	3400		0.00	0.00	
Pyridine	110-86-1	B	0.6	53		0.00	0.00	
n-Octane	111-65-9	B	5	4700		0.00	0.00	
n-Nonane	111-84-2	B	5	3500		0.00	0.00	
propionaldehyde	123-38-6				0.50			0.01
Phosphoric acid tributyl ester	126-73-8	B	0.02	7.3		0.01	0.00	
n-Heptane	142-82-5	B	5	5500		0.00	0.00	
Cyanides, as CN	51-12-5	B	0.2	17	0.5	0.00	0.00	0.00
Carbon tetrachloride	56-23-5	AII	20	0.067		0.00	0.00	
n-Propyl nitrate	627-13-4	B	5	360		0.00	0.00	
Ethyl alcohol	64-17-5	B	5	6300		0.00	0.00	
Methyl alcohol	67-56-1	B	5	870		0.00	0.00	
2-Propanone (Acetone)	67-64-1	B	5	5900		0.00	0.00	

Table 7-2. Source Term Emission Limit Ratio. (2 sheets)

Methane, trichloro-	67-66-3	All	10	0.043	0.45	0.00	0.00	0.00
n-Propyl alcohol	71-23-8	B	5	1600		0.00	0.00	
n-Butanol	71-36-3	B	5	500		0.00	0.00	
Benzene	71-43-2	All	20	0.12	0.50	0.00	0.00	0.00
Methyl chloroform (1,1,1-Trichloroethane)	71-55-6	B	5	6400	0.50	0.00	0.00	0.00
Chloromethane	74-87-3	B	5	340	0.50	0.00	0.00	0.00
Acetonitrile	75-05-8	B	2.6	220	0.50	0.00	0.00	0.01
Acetaldehyde	75-07-0	All	50	0.45		0.00	0.00	
Methane, dichloro-	75-09-2	All	50	0.56	0.50	0.00	0.00	0.00
tert-Butyl alcohol	75-65-0	B	5	1000		0.00	0.00	
Trichlorofluoromethane	75-69-4	B	5	19000		0.00	0.00	
Dichlorodifluoromethane	75-71-8	B	5	16000		0.00	0.00	
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	76-13-1	B	5	27000		0.00	0.00	
Ammonia	7664-41-7	B	2	100		0.00	0.00	
2-Butanone (Methyl ethyl ketone)	78-93-3	B	5	1000	0.50	0.00	0.00	0.01

8.0 CONCLUSIONS AND RECOMMENDATIONS

This study showed that emissions of organic compounds from retrieving the C-200 tanks would be below Washington Administrative Code regulations for Acceptable Source Impact Level that indicates that abatement systems are not required. The use of the simple screening model described in this document would indicate that no compounds would exceed Washington Administrative Code regulations for Small Quantity Emission Rates. The thresholds in WAC-173-401-531 will not be exceeded.

Monitoring per an approved Industrial Hygiene monitoring plan is recommended as a best management practice.

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APPENDIX A

SPREADSHEET OUTPUT

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Table A-1. Tank 241-C-200 Calculations.

(This sheet calculates emissions from C-204 vapor data.)

Chemical Name	Molecular Weight	Chemical ID	TAP Class	C-204 Headspace avg conc (ppbv)	C-204 Headspace avg conc (mg/m^3)	C-200 Emissions lb/hr	C-200 Emission µg/m^3	C-200 Emissions tons/yr
Ethyl benzene	106.17	100-41-4	B	2.73				
Undecane, 3-methyl-	170.341	1002-43-3		372.87				
Butane	58.12	106-97-8	B	209.54				
1,3-Butadiene	54.09	106-99-0	AII	452.09	1.0	2.02E-03	7.11E-04	8.04E-03
Propanenitrile	55.0799	107-12-0		38.68	0.1	1.76E-04		7.00E-04
Methyl isobutyl ketone	100.16	108-10-1	B	6.08	0.0	5.03E-05	5.03E-07	2.00E-04
Benzene, methyl-	92.14	108-88-3	B	46.65	0.2	3.55E-04	3.55E-06	1.41E-03
Cyclohexanone	98.15	108-94-1	B	22.56	0.1	1.83E-04	1.83E-06	7.28E-04
Pentane	72.15	109-66-0	B	13.60	0.0	8.11E-05	8.11E-07	3.23E-04
Butanenitrile	69.107	109-74-0		83.85	0.2	4.79E-04		1.90E-03
Furan, tetrahydro-	72.11	109-99-9	B	45.75	0.1	2.73E-04	2.73E-06	1.08E-03
Hexane (n-hexane)	86.18	110-54-3	B	13.84	0.0	9.85E-05	9.85E-07	3.92E-04
Pentanenitrile	83.1341	110-59-8		2.14	0.0	1.47E-05		5.86E-05
Cyclohexane	84.16	110-82-7	B	17.87	0.1	1.24E-04	1.24E-06	4.94E-04
Pyridine	79.10	110-86-1	B	1.69	0.0	1.11E-05	1.11E-07	4.40E-05
Octane	114.23	111-65-9	B	10.16	0.0	9.59E-05	9.59E-07	3.82E-04
Nonane	128.26	111-84-2	B	10.21	0.1	1.08E-04	1.08E-06	4.31E-04
Dodecane	170.34	112-40-3		1819.30	12.9	2.56E-02		1.02E-01
Undecane	156.31	1120-21-4		556.63	3.6	7.19E-03		2.86E-02
1-Octadecanol	270.5029	112-92-5		1437.77	16.2	3.21E-02		1.28E-01
1-Propene	42.08	115-07-1		317.51	0.6	1.10E-03		4.39E-03
1-Propene, 2-methyl-	56.11	115-11-7		147.67	0.3	6.84E-04		2.72E-03
Propionaldehyde	58.08	123-38-6		324.11	0.8	1.55E-03		6.19E-03
Butanal	72.11	123-72-8		6.70	0.0	3.99E-05		1.59E-04
Decane	142.29	124-18-5		182.79	1.1	2.15E-03		8.55E-03
Phosphoric acid tributyl ester	266.32	126-73-8	B	6.88	0.1	1.51E-04	1.51E-06	6.02E-04
Tridecane, 6-methyl-	198.3952	13287-21-3		473.02	3.9	7.75E-03		3.08E-02
Heptane	100.21	142-82-5	B	20.50	0.1	1.70E-04	1.70E-06	6.75E-04
Cyanides, as CN	26.00	51-12-5	B	179.25	0.2	3.85E-04	3.85E-06	1.53E-03
Carbon tetrachloride	153.82	56-23-5	AII	0.22	0.0	2.85E-06	1.00E-06	1.13E-05
Butane, 1-nitro-	103.1218	627-05-4		689.31	3.0	5.87E-03		2.34E-02
n-Propyl nitrate	105.09	627-13-4	B	279.26	1.2	2.42E-03	2.42E-05	9.65E-03
Hexanenitrile	97.1612	628-73-9		2.98	0.0	2.39E-05		9.50E-05
Tridecane	184.3681	629-50-5		1710.30	13.1	2.60E-02		1.04E-01
Tetradecane	198.40	629-59-4		636.78	5.3	1.04E-02		4.15E-02
Ethanol	46.0695	64-17-5	B	286.74	0.6	1.09E-03	1.09E-05	4.34E-03
Methanol	32.0424	67-56-1	B	468.48	0.6	1.24E-03	1.24E-05	4.93E-03
2-Propanone	58.08	67-64-1	B	727.11	1.8	3.49E-03	3.49E-05	1.39E-02
Methane, trichloro-	119.38	67-66-3	AII	0.89	0.0	8.76E-06	3.08E-06	3.49E-05
1-Propanol	60.0966	71-23-8	B	508.84	1.3	2.53E-03	2.53E-05	1.01E-02
1-Butanol	74.12	71-36-3	B	1443.43	4.5	8.84E-03	8.84E-05	3.52E-02
Benzene	78.11	71-43-2	AII	3.67	0.0	2.37E-05	8.34E-06	9.43E-05
Ethane, 1,1,1-trichloro-	133.4052	71-55-6	B	0.90	0.0	9.96E-06	9.96E-08	3.97E-05
Methane, chloro-	50.49	74-87-3	B	6.22	0.0	2.60E-05	2.60E-07	1.03E-04
Acetonitrile	41.05	75-05-8	B	202.07	0.3	6.85E-04	6.85E-06	2.73E-03
Acetaldehyde	44.05	75-07-0	AII	146.83	0.3	5.34E-04	1.88E-04	2.13E-03
Methane, dichloro-	84.93	75-09-2	AII	21.53	0.1	1.51E-04	5.31E-05	6.01E-04
tert-Butyl alcohol	74.12	75-65-0	B	14.15	0.0	8.66E-05	8.66E-07	3.45E-04
Ethane, 1-chloro-1,1-difluoro-	100.496	75-68-3		219.28	0.9	1.82E-03		7.24E-03
Methane, trichlorofluoro-	137.37	75-69-4	B	6.81	0.0	7.72E-05	7.73E-07	3.07E-04
Methane, dichlorodifluoro-	120.91	75-71-8	B	3.89	0.0	3.88E-05	3.88E-07	1.55E-04
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	187.38	76-13-1	B	27.21	0.2	4.21E-04	4.21E-06	1.68E-03
Ammonia	17.0306	7664-41-7	B	0.95	0.0	1.34E-06	1.34E-08	5.32E-06
2-Butanone	72.11	78-93-3	B	218.65	0.7	1.30E-03	1.30E-05	5.18E-03

Table A-2. Assumptions.

Assump ==> this sheet lists all assumptions made

1) Concentrations were increased by 2X standard deviation. Standard deviation of 20% assumed if none available

2) Dispersion factor annual 200E = 7.93E-02 $(\mu g/m^3)/(g/s)$

3) Dispersion factor 24 hour 200E = 2.79 $(\mu g/m^3)/(g/s)$

4) Organic contents of the C-200 tanks are bounded by C-204 vapor sample (C-204 had oily sludge on rag).

5) Vapor in tank 241-C-204 was in equilibrium with sludge when sampled. Vapor concentrations measured in tank 241-C-204 reflect equilibrium vapor pressures of pollutants in sludge matrix.

6) Sludge is intimately mixed with conveying air. Conveying air is in equilibrium with sludge. Pollutants at equilibrium vapor pressure in air exiting vacuum tank (neglecting depletion of pollutants from sludge).

7) Gas discharge rate = 900 std m^3/hr (does not account for falloff in flowrate with increasing vacuum).

8) Vapors behave as ideal gases with a molar volume of 24 liters per mole. Conversions then become:
mg/m^3 = ppbv x mol wt / 24/1000 ppbv = mg/m^3 * 24 * 1000 / mol wt

APPENDIX B

VERIFICATION OF SPREADSHEET

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CALCULATION OF ORGANIC EMISSIONS

B1.0 OBJECTIVE/PURPOSE

The objective of this appendix is to calculate the organic emissions that will occur during waste retrieval from tank 241-C-104. A spreadsheet was used to convert tank headspace vapor sample data and tank condensed phase sample data to stack emissions.

B2.0 METHODS OF ANALYSIS

The definitions and equations used to calculate the organic emissions are presented in this section. Each of the worksheets contained in the organic emission spreadsheet is presented.

B2.1 SOURCE TERM EMISSION LIMIT RATIO

This worksheet compares the calculated organic emission concentration to the regulatory limit by calculating a ratio. Ratios less than one indicate compliance. Data are imported from the worksheet "Regulated Compounds" for TAP class, SQER, ASIL, and Threshold limits. Data are also imported from worksheet "C104 calc."

SQER ratios are calculated by the equation (H5):

=+' C104 calc '!H7/'Sourceterm emission limit ratio'!E5.

For Ethyl benzene CAS# 100-41-4, the source term is 2.40E-5 lb/hr and the SQER is 5 lbs/hr:

2.40E-5/5 = 4.80E-6.

Other compounds are calculated similarly.

ASIL ratios are calculated by the equation (I5):

=+'C104 calc'!I7/'Sourceterm emission limit ratio'!F5.

For Ethyl benzene CAS# 100-41-4, the source term is 2.40E-7 and the ASIL is 1000:

2.40E-7/1000 = 2.40E-10.

Other compounds are calculated similarly.

Threshold ratios are calculated by the Equation J5:

> ==IF(ISNUMBER('C204 calc'!J7/'Sourceterm emission limit ratio'!G5),'C204 calc'!J7/'Sourceterm emission limit ratio'!G5,"")

For Ethyl benzene CAS# 100-41-4, the source term is 9.54E-5 tons/year and WAC 174-460-501 Threshold is 0.5 tons/year:

> 7.45E-5/0.5 = 1.49E-4 (note that the formula returns a blank result if there is no numeric Threshold value)

Other compounds are calculated similarly.

B2.2 C-204 Calculation

This worksheet calculates the organic vapors emission source term for tank 241-C-204.

Data are imported from worksheets "C-204 vapor data," "Regulated Compounds," and "Assump". Tank 241-C-204 headspace average concentrations are imported from worksheet "C-204 vapor data." Constants and assumed values used in the calculations are imported from work sheet "Assump." Properties of the regulated compounds are imported from worksheet "Regulated Compounds." Calculations performed by the worksheet are listed below.

Headspace average concentration was calculated by five different equations:

1. Headspace concentration from TWINS data worksheet "C-204 vapor data" results in mg/m^3 plus assumed data variability and convert mg/m^3 to ppbv (F26):

   =(AVERAGE('C204 vapor data'!G211)*(1+2*Assump!$J$3))*24*1000/C26

   where:

   AVERAGE('C204 vapor data'!G211) = 11.575 mg/m^3 for 1-Octadecanol CAS# '112-92-5, where only 1 detected result is available,

   Assump!$J$3 = assumed 20% standard deviation - used if no standard deviation can be calculated from the data, and

   C26 = molecular weight = 270.5029 for Octadecanol CAS# '112-92-5,

   Multiplying by 24 * 1000 and dividing by molecular weight to convert mg/m^3 per Assumption 8.

(11.575*(1+2*0.2))*24*1000/270.5029 = 1437.77 ppbv.

Other compounds are calculated similarly.

2. Headspace average concentration from TWINS data worksheet "C-204 vapor data" in ppbv plus assumed data variability (F36):

   =(AVERAGE('C204 vapor data'!G315)*(1+2*Assump!$J$3))

   where:

   AVERAGE('C204 vapor data'!G315) = 0.16 ppv, the only detected result for carbon tetrachloride CAS# 56-23-5,

   Assump!$J$3 = data variability. Assumed standard deviation of 20% - used because no standard deviation is available, and

   0.16*(1+2*0.2) = 0.22 ppbv

Other compounds are calculated similarly.

3. Headspace concentration from TWINS data worksheet "C-204 vapor data" in ppbv plus measured data variability (F7):

   =(AVERAGE('C204 vapor data'!G18:G23)+2*STDEV('C204 vapor data'!G18:G23))

   where:

   'C204 vapor data'!G18:G23 = 2.5, 1.8, 1.5, 1, 0.92, and 0.76 ppv for ethylbenzene CAS# 41-100-4,

   AVERAGE('C204 vapor data'!G18:G23) is the average of the 6 measurements for ethylbenzene CAS# 41-100-4

   AVERAGE('C204 vapor data'!G18:G23) = (2.5+1.8+1.5+1+0.92+0.76)/6, which is 1.413 ppbv for ethylbenzene CAS# 41-100-4

   STDEV('C204 vapor data'!G18:G23) is the standard deviation of the 6 measurements of ethylbenzene CAS#41-100-4

   STDEV(2.5+1.8+1.5+1+0.92+0.76) = 0.66 ppbv

   1.413 ppbv + 2 * 0.66 ppbv = 2.73 ppbv.

Other compounds are calculated similarly.

4. Headspace average concentration from TWINS data (worksheet "C204 data") in mg/m^3 plus measured data variability with conversion from mg/m^3 to ppbv by equation (F8):

   =(AVERAGE('C204 vapor data'!G6:G8)+2*STDEV('C204 vapor data'!G6:G8))*24*1000/C8

   where:

   'C204 vapor data'!G6:G8 = 2.072, 1.846, and 1.155 mg/m^3 from TWINS data for Undecane, 3-methyl-, CAS# 1002-43-3

   C8 = molecular weight = 170.342 for Undecane, 3-methyl-, CAS# 1002-43-3,

   STDEV('C204 vapor data'!G6:G8) = the standard deviation of 2.072, 1.846, and 1.155 mg/m^3 = 0.4777 mg/m^3,

   Multiplying by 24 * 1000 and dividing by molecular weight to convert mg/m^3 in accordance with Assumption 8.

   ((2.072+1.846+1.155)/3 +2*0.4777)*24*1000/170.342 = 372.87 ppbv.

Other compounds are calculated similarly.

5. Headspace average concentration of cyanide as CN from TWINS data (worksheet "204 data") for nitriles by Equation F35:

   ==SUM(F11*C35/C11,F16*C35/C16,F19*C35/C19,F39*C35/C39,F51*C35/C51)

   where:

   F11 = 38.68 ppbv, the average propane nitrile concentration adjusted for the standard deviation as described above,

   C35 = 26, the molecular weight of cyanide,

   C11 = 55.0799, the molecular weight of propane nitrile, so that

   F11*C35/C11 is the contribution of propanenitrile to total cyanide in ppv.

   The remaining terms in the summation are similarly the contributions to total cyanide from butanenitrile, pentanenitrile, hexanenitrile, and acetonitrile, respectively.

Tank 241-C-204 headspace estimated concentration in mg/m^3 is obtained from the C-204 headspace average concentration in ppbv by Equation G24:

=F24*C24/(24*1000)

where:

F24 = 1819.30 ppbv for dodecane CAS# 112-40-3

C24 = 170.34 g/mole, the molecular weight of dodecane CAS# 112-40-3

the factor 1/(24*1000) is a unit conversion from ppbv to mole fraction, milligrams to grams and moles to cubic meters at standard conditions per Assumption 8

1819.30 * 170.34 / (24*1000) = 12.9 mg/m^3

Other compounds are calculated similarly.

Source terms in pounds per hour are calculated by Equation H24:

=Assump!$C$17*G24/(454*1000)

which is (m^3 per hour of air exhausted from the AMS and vacuum tank by the vacuum pump) times (equilibrium concentration of each organic compound in headspace)

where:

Assump!$C$17 = 900 m^3/hr per Assumption 7

G24 = concentration of organic compound in tank 241-C-204 which is 12.9 mg/m^3 for dodecane CAS # 112-40-3,

The divisor (454*1000) is a conversion from milligrams to grams and from grams to pounds.

900*12.9/(454*1000) = 2.56E-2 pounds per hour.

Other compounds are calculated similarly.

Tank 241-C-104 ASIL emission in μg/m^3 for TAP Class B compounds are 24-hour averages or annual averages depending on the TAP class, calculated by Equation I47:

=IF(LEFT(E47)="B",Assump!$C$17*G47/3600/1000*Assump!$E$5,
IF(LEFT(E47)="A",Assump!$C$17*G47/3600/1000*Assump!$E$7,""))

which is a branching statement in which the emissions are calculated as follows if the compound is identified as a toxic class B. For example, the first character is cell E47 is a "B"), so the branching statement selects the following expression:

Assump!$C$17*G47/3600/1000*Assump!$E$5 which is

(m^3/hr of air from the AMS and vacuum tank) times (concentration of organic compound) divided by (3600 seconds per hour) divided by (1000 g/mg) times (dispersion factor).

where:

Assump!$C$17 = 900 m^3/hr capacity of vacuum pump

G47 = concentration of organic compound in tank 241-C-204 which is 4.5 mg/m^3 for 1-butanol CAS # 71-36-3,

Assump!$E$7 = 2.79 (μg/m^3)/(g/s) which is the dispersion factor

900*4.5/3600/1000*2.79 = 8.84E-05 μg/m^3.

The branching statement calculates annual averages when the compound is identified as a toxic class AII. The tank 241-C-204 vapor samples did not contain detected concentrations of toxic class AIII compounds. For acetaldehyde CAS# 75-07-0, the toxic class in cell E52 is "AII" and the first character of cell E52 is "A" so the branching statement in Equation I52 selects the following equation:

=IF(LEFT(E52)="B",Assump!$C$17*G52/3600/1000*Assump!$E$5,
IF(LEFT(E52)="A",Assump!$C$17*G52/3600/1000*Assump!$E$7,""))

and the ASIL is calculated according to :

Assump!$C$17*G52/3600/1000*Assump!$E$7, which is

(m^3/hr of air from the AMS and vacuum tank) times (concentration of organic compound) divided by (3600 seconds per hour) divided by (1000 g/mg) times (dispersion factor).

where:

Assump!$C$17 = 900 m^3/hr capacity of vacuum pump

G52 = concentration of organic compound in tank 241-C-204 which is 0.2695 mg/m^3 for acetaldehyde CAS # 75-07-0,

Assump!$E$5 = 7.39 E-02 (μg/m^3)/(g/s) which is the dispersion factor

900*0.2697/3600/1000*7.39E-02 = 1.88E-04 μg/m^3.

The branching statement produces no result for compounds which are neither class AII nor B.

Other compounds are calculated similarly.

Source terms in tons per year are calculated by Equation G24:

=G24*Assump!$C$17/1000/1000/1000*24*365.25

where:

G24 = concentration of organic compound in tank 241-C-204 which is 12.9 mg/m^3 for dodecane CAS # 112-40-3,

Assump!$C$17 = vacuum pump flowrate from vacuum tank and AMS, 900 m^3/hr

1000, 1000, and 1000 are conversions from mg to g, g to kg, and kg to ton

24 and 365.24 are conversions from hours to days and days to years, respectively.

12.9*900/1000/1000/1000*24*365.25 = 1.02E-01 tons per year.

Other compounds are calculated similarly.

B2.3 REGULATED COMPOUNDS

This sheet compiles all of the regulated compounds from the WAC codes listed in later worksheets and sorts the compounds by CAS number. TAP class is taken from WAC 173-460-160 for class B TAP and ASILs and WAC 173-460-150 for class A Toxic Air Pollutants (AII - Annual Average, B - 24hr Average, and AIII - 24hr Average). SQER is taken from WAC-173-460-080 demonstrating ambient impact compliance. ASIL is taken from WAC 173-460-160 for class B TAP and ASILs and WAC-173-460-150 for class A Toxic Air Pollutants. Threshold levels are taken from WAC 173-401-531 Thresholds for hazardous air pollutants.

B2.4 ASSUMPTIONS

This worksheet collects the assumptions used by all of the worksheets to develop the organic pollutant emission source term.

The following assumptions were made and used throughout the spreadsheet:

1. Organic concentration data from TWINS vapor sampling was increased by 2 times the standard deviation or by 20 percent (cell J5) if no standard deviation was available.

2. The headspace organic vapors in tank 241-C-204 were at equilibrium with the sludge layer at the time of sampling, and these sample results bound the organic vapor concentrations during the retrieval of all four C-200 tanks.

   No more than 900 m^3/hr of air will be drawn through the AMS, pneumatic conveying tube, and vacuum tank.

3. The 900 m^3/hr of air drawn through the AMS, pneumatic conveying line, and vacuum tank, will achieve the same equilibrium organic vapor concentration throughout the duration of the retrieval activity as was observed in the tank C-204 vapor samples.

4. The organic pollutants and ammonia entrained in the 900 m^3/hr of air drawn through the AMS, pneumatic conveying line, and vacuum tank comprise essentially all the pollutant emissions during the retrieval activity. Other paths to transport these pollutants from the sludge to the environment are negligible in comparison.

5. At the low pressures and vapor concentrations, the organic pollutants and ammonia behave essentially as ideal gases in the vapor phase. Conversion from parts per billion by volume (ppbv) to mg/m3 then becomes merely:

   mg pollutant/m^3 = ppbv times (1 E-09 mole pollutant per mole total per ppbv) times (molecular weight g/mole pollutant) times (mole total per 24 liters at standard conditions) times (1000 liters per m^3) times (1000 mg/g)

   mg/m^3 = ppbv times molecular weight /24 /1000

   Conversely, the conversion from mg/m^3 to ppv becomes:

   ppv = mg/m^3 * 24 8 1000 / molecular weight.

B2.8 WAC 173-460-160

This sheet lists regulatory information from WAC 173-460-160 class B TAP and ASILs.

B2.9 WAC 173-460-150

This sheet lists regulatory information from WAC 173-460-150 Class A Toxic Air Pollutants.

B2.10 WAC 173-460-080

This sheet lists regulatory information from WAC 173-460-080 Thresholds for hazardous air pollutants.

B2.11 WAC 173-401-531

This sheet lists regulatory information from WAC 173-401-531.

B2.15 C-204 VAPOR DATA

This worksheet lists data from tank 241-C-204 TWINS vapor characterization analysis report January 13, 2003. The data are sorted by CAS# for convenience.

B3.0 REFERENCES

WAC 173-401, 2002, "Operating Permit Regulation," *Washington Administrative Code*, as amended.

WAC 173-460, 1998, "Controls for New Sources of Toxic Air Pollutants," *Washington Administrative Code*, as amended.